Supporting Information

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A naphthalimide-based 'Pourbaix sensor': a redox and pH driven AND logic gate with photoinduced electron transfer and internal charge transfer mechanisms

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Experimental

Instrumentation

Melting points were recorded on a Stuart Griffin melting point with a Fisherbrand UK thermometer apparatus. The apparatus was calibrated against pure samples of caffeine and vanillin. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker AM 250 NMR spectrometer at 250.1 MHz equipped with a $^{1}H/^{13}C$ dual probe at room temperature. Samples of approximately 7 mg were dissolved in 0.8 mL of chloroform-*d*. Raw data from the instrumentation were processed on a Bruker Aspect 3000 compute using 16K complex points. Chemical shifts are reported in ppm versus tetramethylsilane at δ = 0.00 ppm. Infra-red spectra were recorded using a Shimadzu IR-Affinity 1 spectrometer. Prior to use the instrument was calibrated against a 1602 cm^{-1} polystyrene absorption spectrum. IR analyses were done as either as KBr disks or as a thin film between NaCl plates depending on the sample under investigation. UV-visible absorption spectra were recorded on a Jasco V-650 spectrophotometer interfaced to a desktop computer using a medium response, a bandwidth of 2 nm and a scan speed of 500 nm min^{-1}. Samples were scanned from 350 to 520 nm. All spectra were corrected for the solvent by scanning the solvent blank prior to the experiments. Fluorimetric studies were performed on a Jasco FP-8300 spectrophotometer in emission mode at an excitation wavelength of 399 nm, a bandwidth of 2.5 nm for both slits and a scan speed of 500 nm min^{-1}. Samples were scanned from 420 to 670 nm. Electrospray time-of-flight (ES-TOF) spectra were performed on a Waters LC Premier instrument.

Synthesis

Synthesis of **3** – Ferrocenylmethylamine

Ferrocenylmethylamine **3** was prepared according to a two-step literature procedure.[S1] Ferrocenecarboxaldehyde **2** (1.06 g, 4.95 mmol) and hydroxylamine (0.652 g, 19.8 mmol) were dissolved in 30 mL ethanol and refluxed for 4 hours at 90 °C. The reaction was monitored using TLC using petroleum ether and diethyl ether (3:7) as eluent. Consequently, the oxime was mixed with 50 mL of water and extracted with

dichloromethane (3×30 mL), dried over anhydrous $MgSO_4$ and the solvent removed under vacuum to yield the oxime as an orange powder.

Ferrocenylmethylamine was synthesised by reacting $LiAlH_4$ (0.756 g, 19.9 mmol) with the oxime in 20 mL of anhydrous THF. The reaction was refluxed at 80 °C for 24 hours and monitored by TLC with petroleum ether and diethyl ether (3:7) as the eluent. The organic phase was extracted in diethyl ether (4×30 mL), dried over $MgSO_4$ and collected by rotary evaporator. The product **3** was purified by flash column chromatography using silica gel and eluted with ethyl acetate and a few drops of triethylamine after removal of other fractions. The amine **3** was collected as the last yellow band. Removal of the solvent by rotatory evaporator gave **3** as an orange oil in 41% yield.

^{1}H-NMR (250 MHz, $CDCl_3$, $SiMe_4$, ppm): δ_H 1.70 (br s, 2H, NH_2), 3.55 (s, 2H, CH_2), 4.15 (m, 9H, Cp); ν_{max} (NaCl/cm^{-1}): 3366, 3298, 3092, 2965, 2926, 2857, 1636, 1558, 1541, 1456, 1449, 1437, 1105, 1037, 1022, 1001, 817.

Synthesis of **4** – *N*-ferrocenyl-4-bromo-1,8-naphthalimide

4-bromo-1,8-naphthalic anhydride (0.440 g, 1.59 mmol) and **3** (0.371 g, 1.73 mmol) were dissolved in 25 mL pyridine. The mixture was stirred and refluxed at 125 °C for 18 hours. The reaction was monitored by TLC using 30:1 CH_2Cl_2/acetone. The anhydride and compound **4** gave R_f values of 0.76 and 0.88, respectively. Column chromatography on silica resulted in an orange solid in 34% yield.

Compound **4**: m.p. 230-233 °C (dec.); ^{1}H-NMR (250 MHz, $CDCl_3$, $SiMe_4$, ppm): δ_H 8.65 (d, ^{1}H, J = 7.3 Hz, naphthalimide), 8.52 (d, 1H, J = 8.5 Hz, naphthalimide), 8.38 (d, 1H, J = 7.9 Hz, naphthalimide), 8.00 (d, 1H, J = 7.9 Hz, naphthalimide), 8.65 (t, 1H, J = 7.3 Hz, naphthalimide), 5.12 (s, 2H, -CH_2), 4.50 (t, 2H, J = 1.8 Hz, Cp), 4.22 (s, 5H, Cp), 4.09 (t, 2H, J = 1.8 Hz, Cp).

Synthesis of **1** – *N*-ferrocenyl-4-methylpiperazine-1,8-naphthalimide

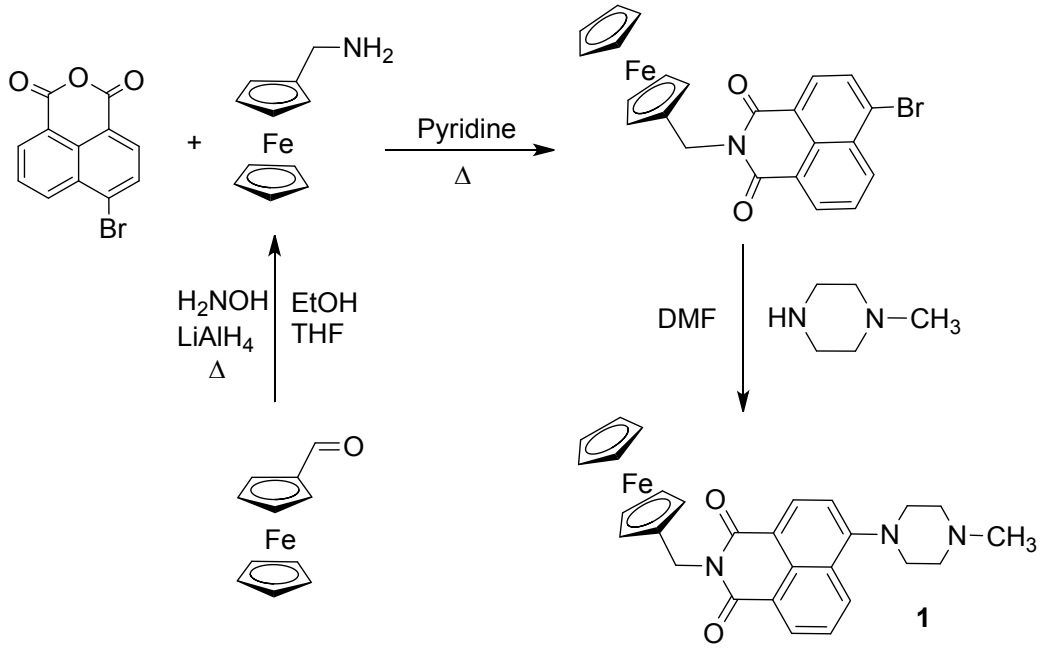
In a 100 mL round-bottomed flask, **4** (209 mg, 0.44 mmol) was dissolved in 20 mL of DMF and 1-methylpiperazine (250 mg, 2.50 mmol).[S2] The reaction mixture was stirred at room temperature under nitrogen for 4 days. Afterwards, 150 mL of water was added to the flask resulting in a yellow precipitate, which was filtered and washed with cold water. Subsequently, the solid was dissolved in hot 3:2 (v/v) EtOH/H_2O, filtered and concentrated. On cooling in an ice bath, a yellow precipitate was recovered by vacuum filtration, which was washed with cold water and diethyl ether and collected in 72% yield.

Compound **1**: m.p. 170 ºC (dec.); ^{1}H NMR (250 MHz, $CDCl_3$, $SiMe_4$, ppm): δ_H 8.56 (d, 1H, J = 7.3 Hz, H_j), 8.49 (d, 1H, J = 7.9 Hz, H_i), 8.37 (d, 1H, J = 8.6 Hz, H_e), 7.65 (t, 1H, J = 7.3 Hz, H_h), 7.19 (d, 1H, J = 8.6 Hz, H_f), 5.11 (s, 2H, -CH_2 spacer), 4.50 (m, 2H, J = 1.8 Hz, Cp), 4.20 (s, 5H, Cp), 4.07 (m, 2H, J = 1.8 Hz, Cp), 3.28 (m, 4H, upper -CH2 methylpiperazine), 2.73 (m, 4H, lower -CH_2 methylpiperazine), 2.42 (s, 3H, -NCH3 methylpiperazine); ^{13}C-NMR (62.9 MHz, $CDCl_3$, $SiMe_4$, ppm): δ_C 39.1, 46.1, 53.0, 55.2, 68.0, 68.6, 70.4, 83.4, 114.9, 116.8, 123.4, 125.6, 126.1, 129.9, 130.2, 131.1, 132.5, 155.9, 163.7, 164.2; ν_{max} (NaCl/cm^{-1}): 3088, 2929, 2837, 2787, 1691, 1654, 1589, 1577, 1558, 1516, 1452, 1419, 1386, 1373, 1334, 1288, 1244, 1139, 1105, 1006, 977, 785; UV-vis (MeOH) λ_{max}/nm (ε/cm^{-1} mol L^{-1}): 399 (12700); UV-vis (1:1 MeOH/H_2O) λ_{max}/nm (ε/cm^{-1} mol L^{-1}): 390 (12000); HRMS Calcd. $C_{28}H_{28}N_3O_2{}^{56}Fe$ [M+H] 494.1524, found 494.1531.

References

(S1) P. D. Beer and D. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1998, 417.

(S2) S. Zheng, P. L. M. Lynch, T. E. Rice, T. S. Moody, H. Q. N. Gunaratne, and A. P. de Silva, *Photochem. Photobiol. Sci*., 2012, **11**, 1675.



Scheme S1 The synthesis of the 'Pourbaix sensor' **1**.

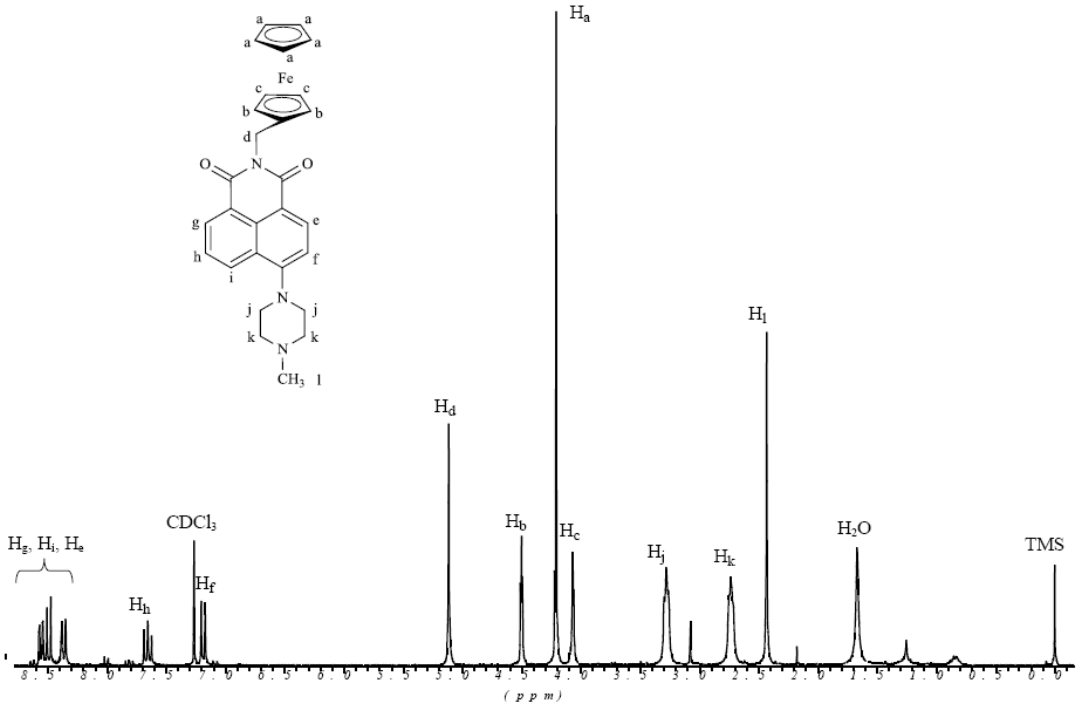


Fig. S1 ^{1}H NMR spectrum of **1** in $CDCl_3$.

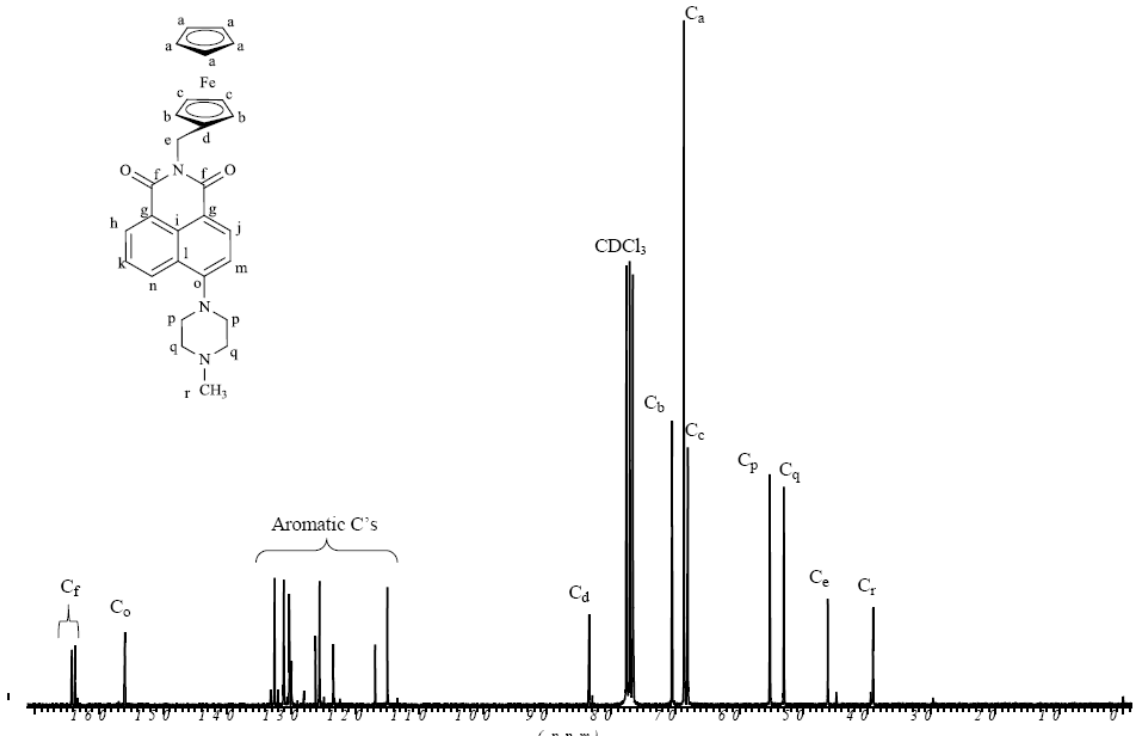


Fig. S2 ^{13}C NMR spectrum of **1** in $CDCl_3$.

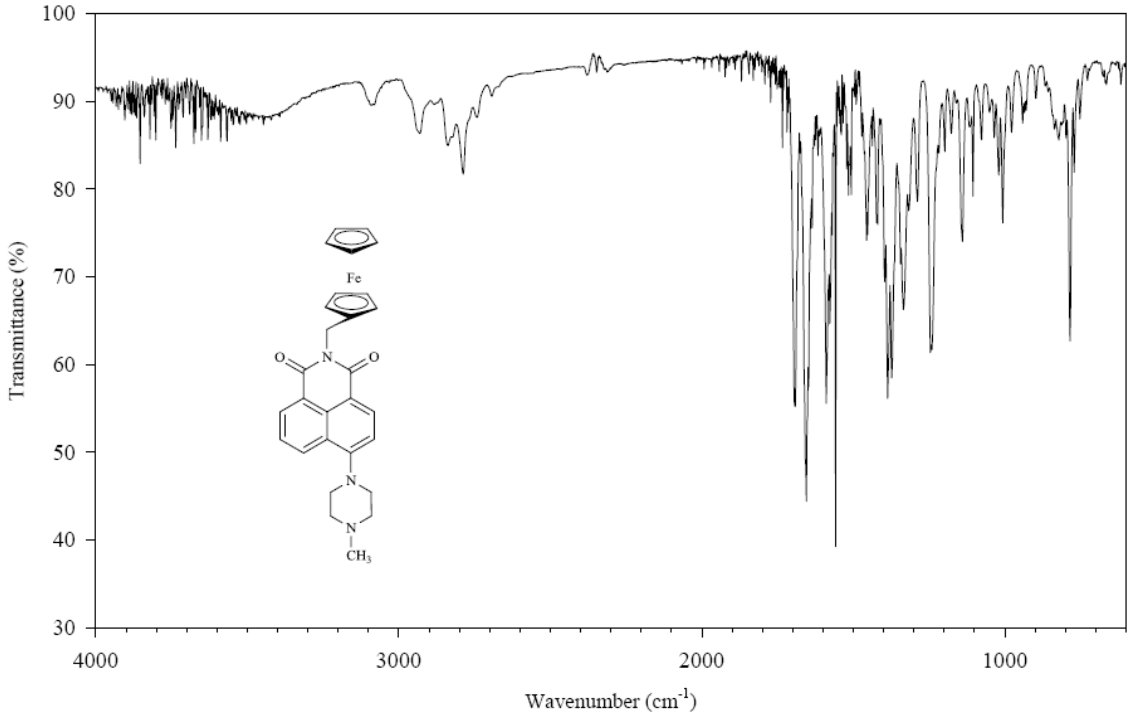


Fig. S3 Infra-red spectrum of **1** as a KBr disk.

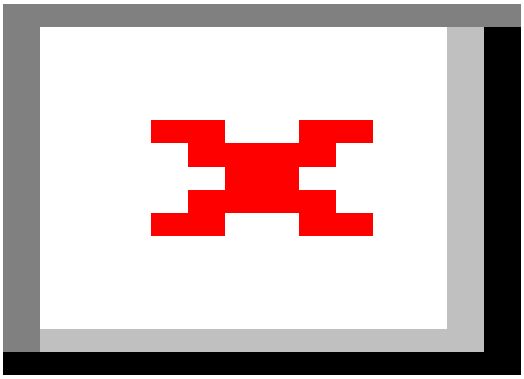


Fig. S4 UV-visible absorption spectra of 10^{-5} M **1** in MeOH in the absence and presence of 25 mM methanesulfonic acid.

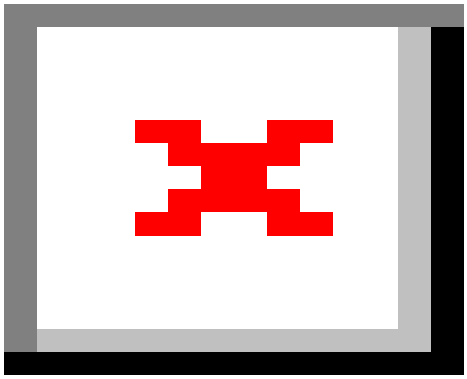


Fig. S5 UV-visible absorption spectra of 10^{-5} M **1** in 1:1 (v/v) MeOH:H_2O with increasing concentration of methanesulfonic acid up to 25 mM.

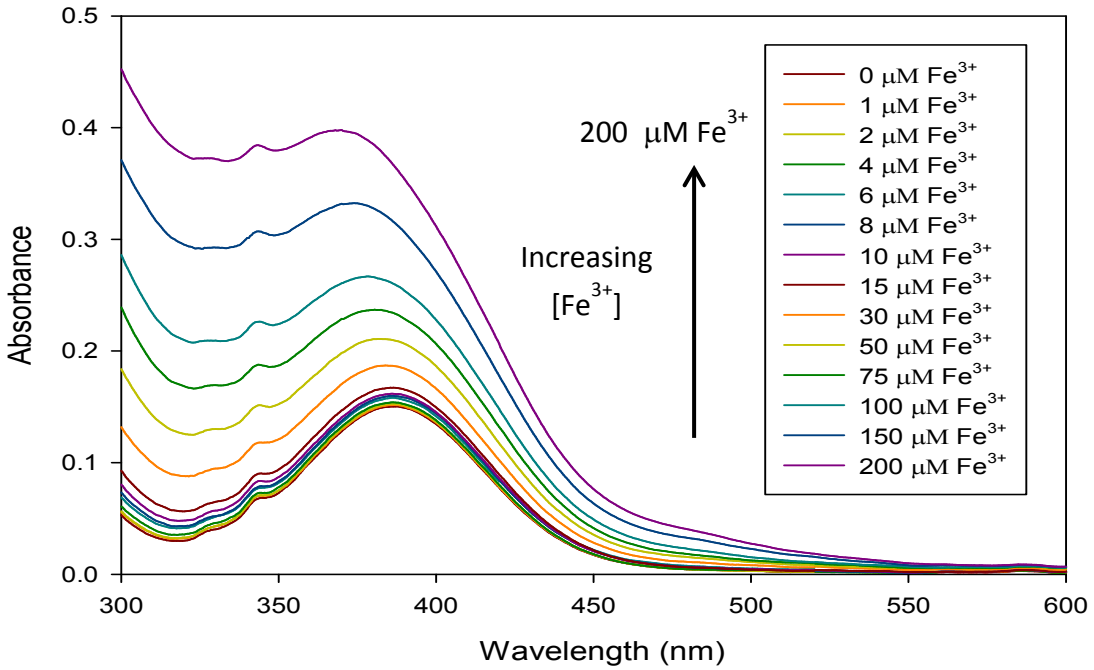


Fig. S6 UV-visible absorption spectra of 10^{-5} M **1** in 1:1 (v/v) MeOH:H_2O at pH 3.6 on increasing concentration of iron(III) sulfate pentahydrate.

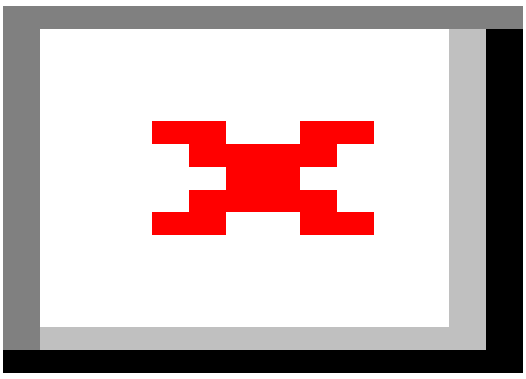


Fig. S7 Fluorescence spectra of **1** in 1:1 (v/v) MeOH:H_2O with methanesulfonic acid as titrant in presence of 20 μM Fe(III).

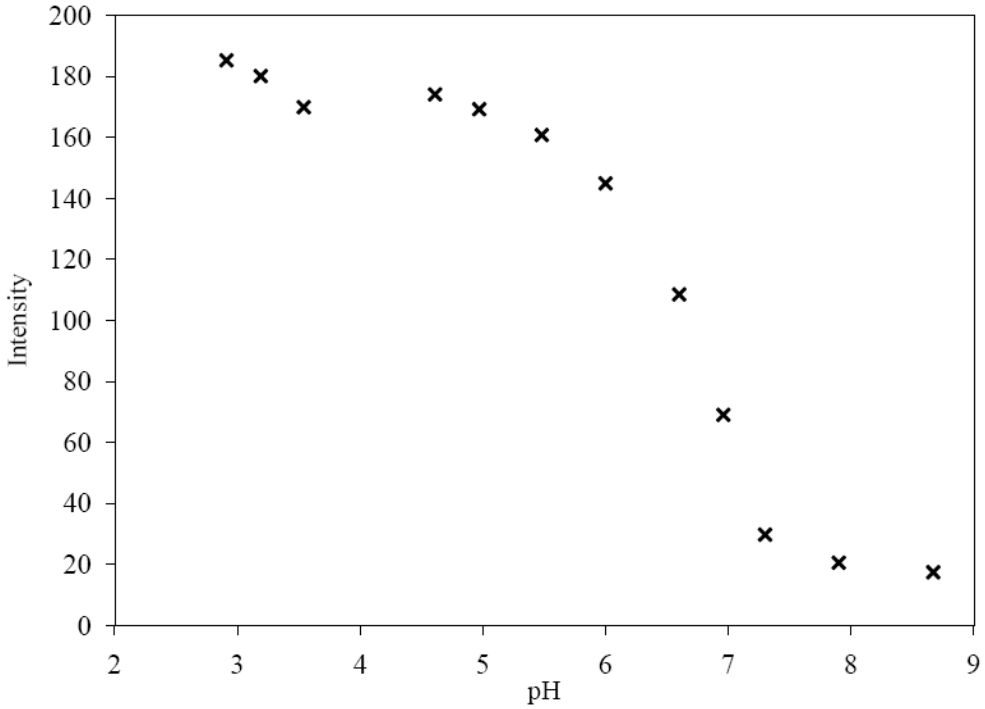


Fig. S8 Titration curve plotted at the maximum intensity of 525 nm against the pH in presence of 20 μM Fe(III) in 1:1 (v/v) MeOH:H_2O.

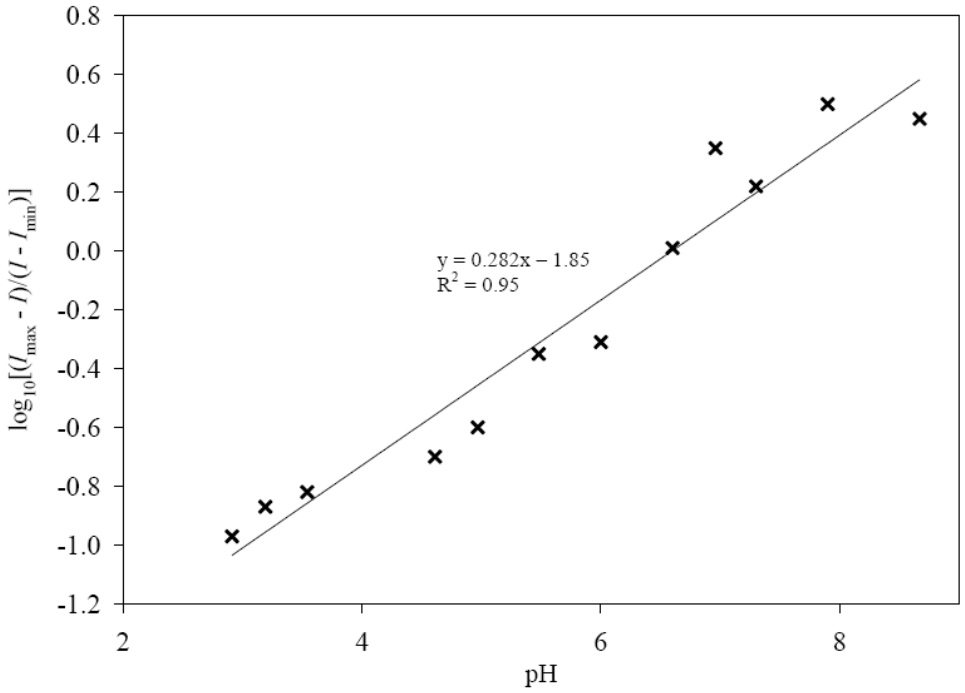


Fig. S9 Graph of $\log[(I_{max} - I)/(I - I_{min})]$ at 525 nm against pH in presence of 20 μM Fe(III) in 1:1 (v/v) MeOH:H_2O.

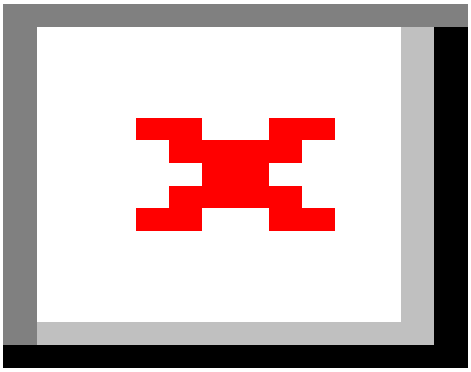


Fig. S10 Fluorescence spectra of **1** in 1:1 (v/v) MeOH:H_2O using Fe(III) as titrant in the presence of 0.20 mM methanesulfonic acid .

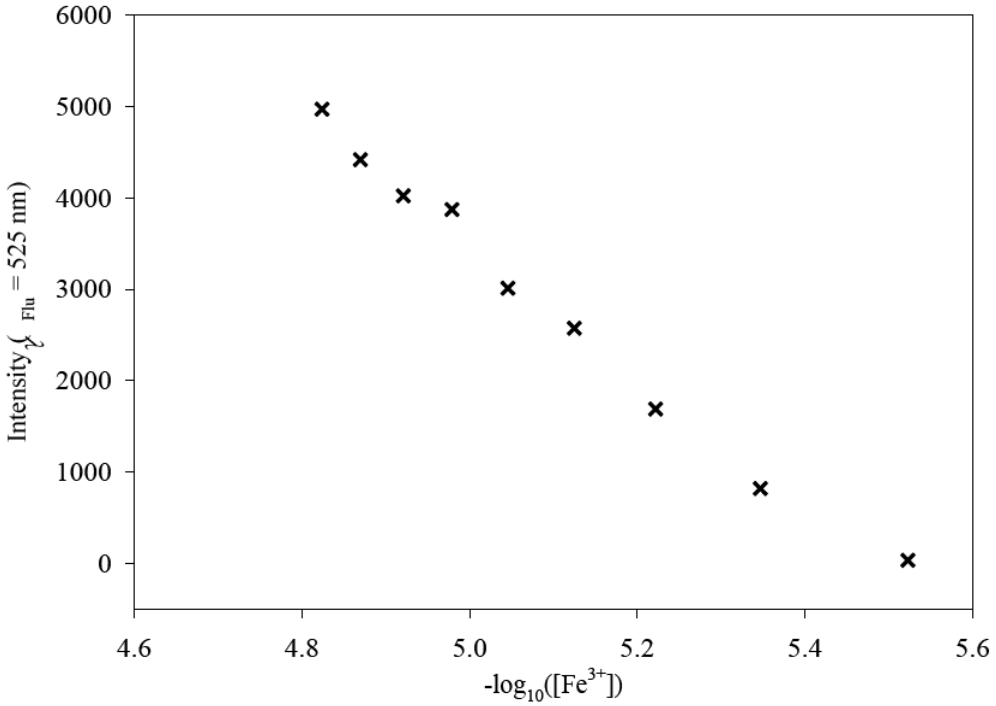


Fig. S11 Fluorescence titration curve plotted at 525 nm against the –log [Fe^{3+}] in the presence of 0.20 mM methanesulfonic acid in 1:1 (v/v) MeOH:H_2O.

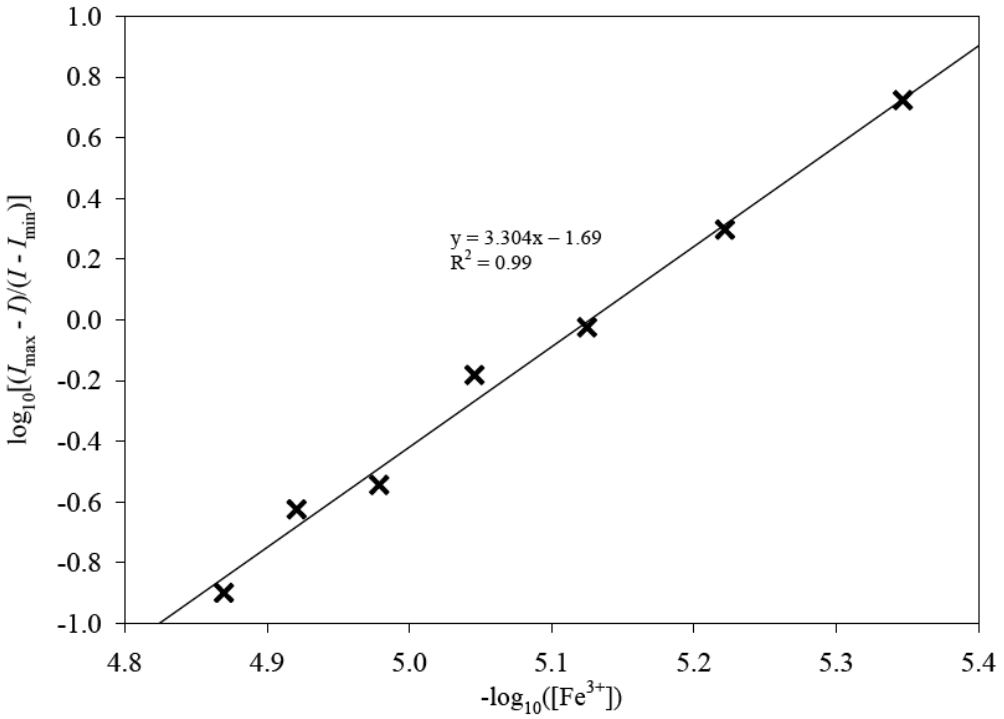


Fig. S12 Plot of $\log[(I_{max} - I)/(I - I_{min})]$ at 525 nm against the $-\log [Fe^{3+}]$ in the presence of 0.20 mM methanesulfonic acid in 1:1 (v/v) MeOH:H_2O.